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Third-order, nonlinear optical interactions of some benzporphyrins

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We measured third-order, nonlinear optical susceptibility $\chi^{(3)}$ for a series of tetrabenzporphyrins in solution in tetrahydrofuran at 532 nm using degenerate four-wave mixing with picosecond pulses and obtained values of molecular second hyperpolarizability $\langle\gamma\rangle$. The corresponding macroscopic $\chi^{(3)}$ values calculated for nine compounds with different substituent groups are four to five orders larger than CS_2. For five of the compounds the $\chi^{(3)}$ values are in the range $1.2\text{–}2.8\times10^{-8}$ esu. Our experiments indicate that the nonlinearity is predominately electronic in origin with a response time faster than the 15 ps resolution of our system.

Organic compounds with π electron delocalization are currently receiving much attention[1,2] for possible device applications in optical communication and optical data processing, in view of their expected large and fast nonlinear optical response.

In this letter we present experimental investigations of third-order nonlinearity for several metallo- and metal-free tetrabenzporphyrin derivatives. They were obtained by synthesis[3,4] as part of an ongoing effort to examine the chemical and physical properties of macrocyclic dye compounds. The tetrabenzporphyrin ring systems can be substituted at their (*meso*) positions with a variety of functional groups. The compounds included in the present study consist of a series of aryl and aliphatic substituents at the *meso* position. In addition to the *meso*-substituted compounds, two examples of tetrabenzporphyrins with substituents in the benzo portion of the molecule are included. One of these is fully fluorinated on the periphery of the tetrabenzo portion of the ring and the other has two methyl substituents on each of the benzo outer rings. In most cases the metal coordinated at the center of the ring is zinc. The chemical structure of the compounds is shown in Fig. 1.

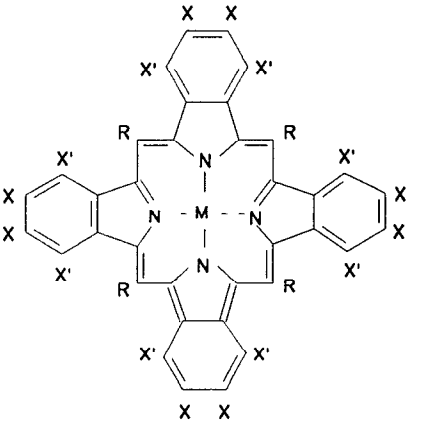
We measured third-order, nonlinear optical susceptibility $\chi^{(3)}$ for all the compounds in solution in tetrahydrofuran (THF) using the technique of degenerate four-wave mixing[5] (DFWM). The source is a Quantel Nd:YAG laser of 1064 nm wavelength frequency-doubled with second harmonic generator (SHG) crystal giving 17 (ps) full width at half maximum (FWHM) single pulses, obtained by mode locking. The average energy of the pulse is 25 mJ. The vertically polarized output at 532 nm is split into three beams, which are temporally and spatially overlapped in the sample contained in 2 or 1 mm cuvettes. The intensity of the phase conjugate beam, proportional to the square of $\chi^{(3)}$, is measured.

In DFWM two intense counter propagating radiation fields $E_1(\omega,t)$, $E_2(\omega,t)$, interact with a third probe beam $E_3(\omega,t)$ in the nonlinear medium to produce the nonlinear polarization P^4_{NL} which is responsible for the fourth beam $E_4(\omega,t)$ phase conjugate of the probe beam. The intensity of the conjugate beam is given by

$$I_4(\omega)=\left(\frac{\omega}{2\epsilon_0 cn^2}\right)^2|\chi^{(3)}|^2 d^2 I_1(\omega)I_2(\omega)I_3(\omega)\cdots, \quad (1)$$

where I_1, I_2, I_3 are the intensities of the forward, backward pumps, and the probe beam, respectively, d is the interaction length, and n the refractive index of the sample.

The susceptibility of the nonlinear medium $\chi^{(3)}$ is obtained by measuring the conjugate beam intensity with a silicon photodiode. The dependence of the phase conjugate intensity on the incident laser intensity is measured and the cubic power dependence is established for CS_2 as well as all the samples studied. Following standard procedure[6,7] direct evaluation of all the parameters in Eq. (1) is avoided by comparison with measurements on a reference sample CS_2 of the same length under identical conditions:



(1) X= X'= Hydrogen; M= Zinc; R= p-Dimethylaminophenyl
(2) X= X'= Hydrogen; M= Zinc; R= Methyl
(3) X= X'= Hydrogen; M= Zinc; R= m-Fluorophenyl
(4) X= X'= Hydrogen; M= Zinc; R= p-Methoxyphenyl
(5) X= X'= Hydrogen; M= Zinc; R= p-Methylphenyl
(6) X= Hydrogen; X'= Methyl; M= Magnesium; R= Hydrogen
(7) X= X'= Hydrogen; M= Zinc; R= Phenyl
(8) X= X'= Fluorine; M= Zinc; R= Hydrogen
(9) X= X'= Hydrogen; M= 2-Hydrogens; R= Hydrogen

FIG. 1. Chemical structure of the compounds.

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TABLE I. Values of $\langle\gamma\rangle$ and $\chi^{(3)}$ for tetrabenzporhyrins.

Compound number	Compound description	$\langle\gamma\rangle 10^{-30}$ esu	$\chi^{(3)} 10^{-8}$ esu
1	Zinc meso-tetra-(*p*-dimethylaminohenyl)tetrabenzporphyrin	10.0	2.8
2	Zinc meso-tetramethyltetrabenzporphyrin	3.3	1.5
3	Zinc meso-tetra-(*m*-fluorophenyl)tetrabenzporphyrin	3.8	1.3
4	Zinc meso-tetra-(*p*-methoxphenyl)tetrabenzporphyrin	4.8	1.4
5	Zinc meso-tetra-(*p*-methylphenyl)tetrabenzporphyrin	4.0	1.2
6	Magnesium octamethyltetrabenzporphyrin	1.6	0.8
7	Zinc meso-tetraphenyltetrabenzporphyrin	0.9	0.3
8	Zinc Hexadecafluorotetrabenzporphyrin	0.7	0.2
9	Tetrabenzporphyrin	0.5	0.3

$$\frac{\chi^{(3)}_{\text{sample}}}{\chi^{(3)}_{CS_2}} = \left(\frac{n_{\text{sample}}}{n_{CS_2}}\right)^2 \frac{d\alpha}{1-e^{-\alpha d}} e^{\alpha d/2} \times \left(\frac{I_{\text{sample}}}{I_{CS_2}}\right)^{1/2} \frac{d_{CS_2}}{d_{\text{sample}}} \cdots, \quad (2)$$

where d is the sample length and I is the intensity of the conjugate beam. The equation is applicable only in the power region where the intensity of the signal is dependent on the cubic power of the incident laser beam. We assumed $\chi^{(3)}$ CS_2 as 6.8×10^{-13} esu as reported by Xuan *et al.*[8] using picosecond pulses.

The second hyperpolarizability $\langle\gamma\rangle$ of a molecule in isotropic media is related[9] to third-order macroscopic susceptibility by

$$\langle\gamma\rangle = \frac{\chi^{(3)}}{L^4 N}\cdots, \quad (3)$$

where N is the number density of molecules per mL and L^4 is the local field correction factor given by $[(n^2+2)/3]^4$.

For a solution of noninteracting particles, the effective $\chi^{(3)}$ assuming a pairwise additive model is given by[9]

$$\chi^{(3)}_{\text{solution}} = L^4[N_{\text{solvent}}\gamma_{\text{solvent}} + N_{\text{solute}}\gamma_{\text{solute}}]\cdots, \quad (4)$$

where N_{solute}, N_{solvent} are the number densities of molecules of the solute and solvent.

For dilute solutions $N_{\text{solute}} = AC/M$ we may write

$$\chi^{(3)}_{\text{solution}} = \chi^{(3)}_{\text{solvent}} + (L^4\gamma_{\text{solute}}A/M)C\cdots, \quad (5)$$

where A is Avogadro's number, M is the molecular weight of solute, and C is the concentration of solute in g/mL. The $\chi^{(3)}_{\text{solution}}$ thus follows a linear relationship with respect to the concentration of the solute, at least for dilute solutions. We measured $\chi^{(3)}$ for all samples in tetrahydrofuran solution in the range of concentrations 10^{-5}–10^{-4} g/mL. The linear behavior is observed for all the samples studied. The molecular second hyperpolarizability of the solute $\langle\gamma\rangle$ is obtained from the slope of the plots. The macroscopic susceptibility $\chi^{(3)}$ of the pure compound is then calculated using Eq. (3). The results are listed for all the compounds in Table I. Compound 7 was measured in dichloromethane and *n*-hexane solutions, also yielding about the same value for $\chi^{(3)}$ as in the solvent THF. Optical absorption of the samples (illustrated for one compound in Fig. 2) indicates[3] a strong peak at about 450 nm and a weak one at 640 nm. The samples are all transparent in the green region of the spectrum. The measured susceptibilities for all the compounds are high—four to five orders larger than CS_2. For five of the compounds the $\chi^{(3)}$ values are in the range $1.2-2.8\times 10^{-8}$ esu, comparable to some of the extremely large values reported in recent literature.[10] Though our optical absorption measurements at low powers indicate the absence of significant resonant contribution to $\chi^{(3)}$, it is quite probable that two photon or other nonlinear process at high intensities may give rise to a resonant contribution, as was observed[11] in some similar compounds.

The nonlinearity of the samples may be due to both electronic as well as nuclear orientation factors. The relative magnitudes can be determined by varying the probe beam polarization, taking advantage of the lower symmetry of orientational nonlinearity compared with the electronic hyperpolarizability. By changing the probe polarization from parallel to perpendicular orientation with respect to the pump beams, the phase conjugate beam intensity should drop by a factor $(\chi^{(3)}_{xxxx}/\chi^{(3)}_{yxxy})^2 = 1/9$ for purely electronic hyperpolarizability and 9/16 for purely orientational nonlinearity.[7,10] By measuring the ratio of the signals for the conjugate beam for parallel and perpendicular probe polarizations, one can estimate the ratio of orientation and electronic contributions. Our observations show that for all the compounds studied the signal dropped to about 1/9, indicating the nonlinearity is predominantly electronic in origin and hence isotropic with extremely fast

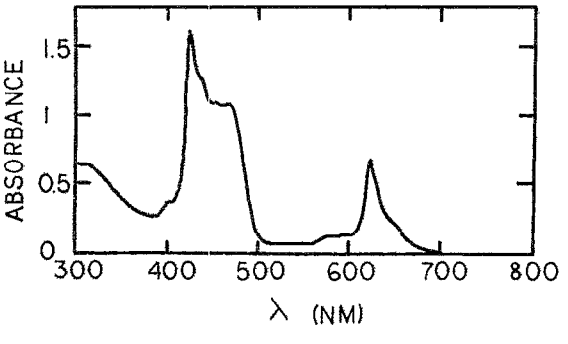

FIG. 2. Optical absorption spectrum of zinc meso-tetra-(*p*-dimethylaminophenyl) tetra benzporphyrin solution in tetrahydrofuran, concentration 0.11 mg/mL.

response time. Time-resolved measurements also support this conclusion. We measured the phase conjugate signal as a function of probe delay with respect to pump beams for all the samples. The curves are symmetric with respect to delay time with FWHM of approximately 15 (ps). The response time is thus found to be shorter than the autocorrelation width, indicating that it is limited by the laser pulse width.

With the limited measurements presently available, it is premature to attach much significance to structure—property interpretations for these compounds. However, a trend has been observed for the compounds having electron donating groups on the *meso*-phenyl substituents of the benzporphyrin macrocycle. Within this series, the stronger donating groups exhibit higher $\chi^{(3)}$ values. This trend follows the Hammett sigma constants reported[12] for substituted aromatic derivatives. We found, interestingly, an approximately linear correlation of $\chi^{(3)}$ with the Hammett constant for the electron donating groups, except for the *m*-fluorophenyl group which has a large positive Hammett constant as well as a high $\chi^{(3)}$ value.

More detailed measurements on solutions and thin films of these and other related compounds are in progress and will be reported soon.

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